Photocatalytic Degradation of Synthetic Dye Wastewater Using Photocatalysts Modified with Coffee Ground-Derived Carbon

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Abstract. *Textile industries discharge large amounts of colored wastewater which is one of the main environmental problems. It affects aquatic ecosystems and the vision of public water resources. Various processes have been developed for the degradation of dye wastewater, one of the most attractive and promising alternative technologies is semiconductor photocatalysis because the reactions can occur at room temperature and pressure. Several studies on photocatalysts, zinc oxide (ZnO) nanoparticles are promising photocatalysts with high photocatalytic activity, biocompatibility, and nontoxicity to human cells. One of the techniques used to enhance the properties of ZnO is doping, especially with carbon (C). Doping the crystal lattice of ZnO with C allows a shift of the bandgap from the UV to the visible light. C can be synthesized from various kinds of waste. Coffee ground waste is one of the interesting C sources. Therefore, it is a good solution to convert coffee ground waste to a C source. In this research, C-doped ZnO was synthesized by a hydrothermal process for the degradation of synthetic dye wastewater (methylene blue). ZnO was modified with C solution (i.e. 10 mL, 20 mL, and 30 mL). The result indicated that the photocatalytic effect of the composites showed a phenomenon of first strengthening and then weakening. The highest photocatalytic degradation was obtained on the C-doped ZnO with an initial C solution of 20 mL. The removal efficiency of color was 91% under visible light.*

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1. Introduction

Textile industries are presently associated with environmental issues due to the consumption of large amounts of water and a variety of chemicals during the dyeing process. Generally, dye wastewater is contaminated with color and chemicals. Also, the negative environmental effects which can include aesthetic problems and aquatic biological processes that change the balance of the ecosystem. The dye-containing effluent is undesirable not only because of colors but also their breakdown products into dangerous characteristics. These are examples of breakdown products formed such as benzidine, naphthalene, and other aromatic compounds. Therefore, it is very important to remediate the dye before discharge into water bodies or the aquatic environment. Nowadays, treatment for dye wastewater is very difficult due to the complexity and recalcitrant nature of the dye. For environmental legislation, the industrial effluent needs an effective process to meet the national quality standard.

Photocatalytic technology is an energy-efficient modern wastewater treatment technology based on the photochemical reaction and catalytic reaction of the catalyst under light conditions. The core of photocatalytic technology is photocatalyst. Many materials have been used as photocatalysts, such as titanium dioxide (TiO_2), zinc oxide (ZnO), tin oxide (SnO_2), zirconium dioxide (ZrO_2), cadmium sulfide (CdS), *etc* [1]. In various photocatalysts, ZnO has attended much attention due to its bandgap (3.3 eV) and chemical stability. The process of photocatalysis is powered by photons that match or exceed the bandgap energy of a given semiconductor. An electron in its valence band (VB) is excited to the conduction band (CB), leaving a positive hole in the VB that forms a hydroxyl radical with the hydroxyl ion in water, which is then available for oxidation. Meanwhile, the excited electron reduces oxygen in the CB, which can also act as an oxidizing agent [2]. Doping on photocatalysts is generally carried out to further reduce the bandgap of the catalysts to make absorption in the visible region and to use sunlight more efficiently. It is suggested that non-metal doping with carbon (C), sulfur (S), or nitrogen (N) would reduce the bandgap in metal oxide photocatalysts [3]. They can significantly expand the

sunlight photo-absorption of wide-band-gap semiconductor materials to visible regions and even a near-infrared region. C is one of the interesting dopants. It can be used as a high-performance photocatalyst. There are various processes to synthesize the C dopant such as hydrothermal processes, laser ablation, arc-discharge, ultrasonication, solvothermal, microwave, and oxygen plasma treatment. The advantages and disadvantages of the different synthetic methods used for the preparation of C dopant are shown in Table 1. The hydrothermal process is an alternative process because it is cost-effective, eco-friendly, non-toxic. In addition, the C dopant can be synthesized from various materials such as commercial vitamin C, sugarcane, and leaves [4,5].

Synthetic Method	Advantage	Disadvantage	Reference
Chemical ablation	Most accessible, various sources	Harsh conditions, drastic processes, multiple steps, poor control oversizes	[6]
Electrochemical carbonization	Size and nanostructure are controllable, stable, one-step	Few small molecule precursors	[7,8]
Laser Ablation	Rapid, effective, surface states tunable	Low QY, poor control over sizes, modification is needed	[9-11]
Microwave irradiation	Rapid, scalable, cost-effective, eco-friendly	Poor control oversizes	[12]
Hydrothermal/ solvothermal treatment	Cost effective, eco-friendly, non-toxic	Poor control oversizes	[13]

Table 1 the advantages and disadvantages of the different synthetic methods used for the preparation of C dopant

In this work, the photocatalytic degradation of dye wastewater (methylene blue) on ZnO photocatalyst under visible light was focused. A waste source, coffee ground, was used as the raw material to synthesize a C dopant for the photocatalyst. The coffee ground was selected as the source of C because it can reduce the cost of material and is easy to collect from the coffee shops. The C dopant is hypothesized to enhance the photocatalytic activity of ZnO under visible light irradiation. Furthermore, the morphology of photocatalysts was analyzed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

2. Methodology

2.1 Chemicals and Materials

The following chemicals and materials that were used for the experiments were hydrogen peroxide (H_2O_2), sodium hydroxide (NaOH), coffee ground, vacuum pump, and glass microfiber filter paper from Whatman (size 6, and 0.22 μm) which were used for the separation of C solution after the hydrothermal process. ZnO commercial powder from Carlo Erba was used as a photocatalyst and photocatalyst modified with C solution. Methylene blue was obtained from Sigma-Aldrich for synthetic dye wastewater.

2.2 Photocatalytic Reactor

The photocatalytic reactor was made of wood (Fig. 1) and divided into two parts. Two fluorescent daylight lamps (18 W) were installed as the irradiation source for each part. There were two magnetic stirrers for each part to obtain the homogeneous samples.

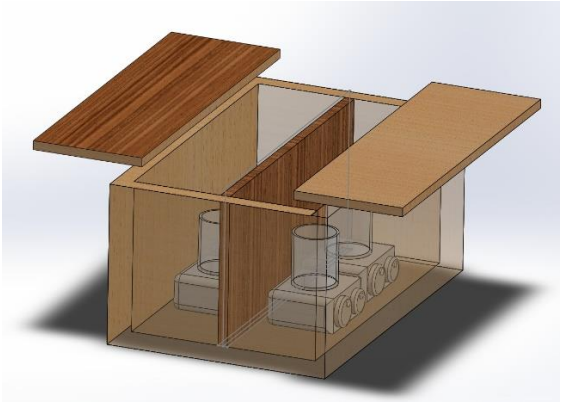

Fig. 1 Photocatalytic reactor; (a) plywood chamber, and (b) magnetic stirrer

2.3 Procedure

In this study, the experiments could be divided into two main parts. In the first part, The C solution was synthesized from the coffee ground via the hydrothermal method. Next, commercial ZnO powder and C solution were synthesized via the hydrothermal method. The obtained photocatalysts were characterized. In the second part, the photocatalytic activities of the photocatalysts were investigated by decolorization of methylene blue in the water.

2.4 Synthesis of C Solution and Modification of ZnO with C Solution

The coffee ground waste was obtained from the coffee shops. The obtained coffee grounds were dried in an oven at 105 °C for 24 h. After that, 15 g of coffee grounds were mixed with NaOH solution, and 100 mL of H_2O_2. The mixed solution was stirred for 2 h. The mixed solution (500 mL) was poured into the vessel of the hydrothermal reactor. The reactor was run at 300 °C for 4 h. Afterward, the solution was cooled down to room temperature and filtered by glass microfiber filter papers to obtain a C solution.

The obtained C solution was added and mixed with 5 g ZnO powder. Afterward, the product was stirred by a magnetic stirrer for 30 min. The prepared photocatalysts

were heated in an oven at 150 °C for 5 h. Next, the obtained photocatalysts were dried in an oven at 105 °C for 24 h and mashed into a powder form. Finally, the obtained photocatalysts were sieved to obtain the same size distribution (150-200 μm)

2.5 Photocatalytic Degradation of Synthetic Dye Wastewater

The photocatalysts (with and without C solution) were investigated for comparison of the dye removal efficiencies. Methylene blue (10 mg/L) was mixed with the obtained photocatalysts in the containers and set up on the magnetic stirrer under the dark condition for the adsorption process. After that, the fluorescent daylight lamps (visible light) were turned on for photocatalytic degradation of synthetic dye wastewater for 6 h. The samples were collected at time intervals of 30, 60, 90, 120, 180, 240, 300, and 360 min and measured absorbance from a spectrophotometer at the wavelength of 664 nm. All experiments were performed in duplicate.

The photocatalysts with various amounts of C solution (10, 20, and 30 mL) were investigated for the dye removal efficiencies. The photocatalysts were mixed with synthetic dye wastewater with the concentration of methylene blue of 10 mg/L and installed inside the reactor. A window of the reactor was completely closed. The reactor was kept in dark condition for a period of time equal to the adsorption equilibrium time. After that, the fluorescent daylight lamps were turned on. The samples in the container were collected every 30 min. All experiments were performed in duplicate.

3. Results and Discussions

The properties and morphology of pure ZnO and C-doped photocatalysts were investigated. The photocatalytic activity of pure ZnO and C-doped photocatalysts were conducted by decolorization of methylene blue under visible light irradiation. The effect of initial quantities of C solution was studied.

3.1 Characterization of Coffee Ground-Derived C Solution

The obtained C solution which was synthesized from coffee grounds by a hydrothermal process is shown in Fig. 2. The C solution was a light-brown color by filtration through a 0.22 μm microporous membrane. The obtained C solution was characterized by transmission electron microscopy. The TEM images of the C solution are shown in Fig. 3. The average diameter of C was 7.8 ± 1.74 nm from a count of 25 C particles. It was found that the size of the C in this work had the same size as C synthesized by Wang et al. (2017) (8 ± 3 nm) [14] and Surendran et al. (2020) (4-13 nm) [5].

Fig. 2 C solution

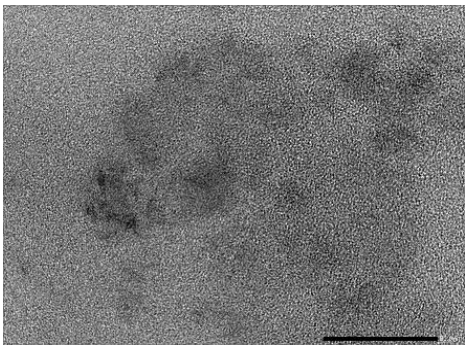

Fig. 3 TEM images of coffee ground-derived C (the scale bar = 50 nm)

3.2 Characterization of ZnO and ZnO modified with C solution

SEM with an accelerating voltage of 20 kV and TEM were used to investigate the surface and crystal morphology of pure ZnO. The results are shown in Fig. 4 (a). Normally, there are three crystal structures of ZnO: hexagonal wurtzite, cubic zinc-blende structure, and a rarely-observed cubic rock-salt (NaCl-type). Under ambient conditions, the most thermodynamically stable structure is the wurtzite form. The zinc-blende structure is metastable and can be stabilized only by epitaxial growth on cubic substrates while the cubic rock-salt structure is usually only stable under extreme pressure [15]**.** The structure of pure ZnO in this study consisted of hexagonal form liked the wurtzite type of ZnO structure, which is more stable under ambient conditions.

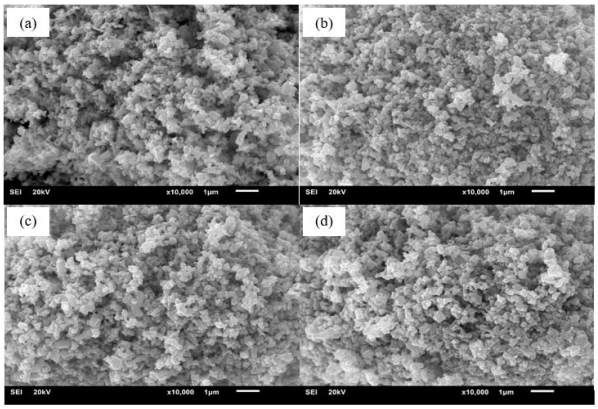

Fig. 4 SEM images of (a) ZnO and C-modified ZnO with various initial amounts of C solutions of (b) 10 mL, (c) 20 mL, and (d) 30 mL.

For ZnO modified with C solution (10 mL, 20 mL, and 30 mL), the results (Fig. 5) showed that the obtained photocatalysts were in powder form with light yellow color. The color of the obtained photocatalysts with 10 mL of C solution was lighter than the color of the obtained photocatalysts with 30 mL of C solution.

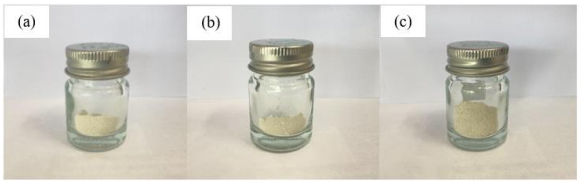

Fig. 5 The obtained C-doped photocatalaysts; (a) 10 mL of C solution, (b) 20 mL of C solution, and (c) 30 mL of C solution

The obtained photocatalysts (10 mL, 20 mL, and 30 mL of C solutions) were characterized by SEM. The results are shown in Fig. 4(b)-4(d). The obtained C-modified ZnO with all conditions had a hexagonal form like the wurtzite type, which was similar to the pure ZnO, because the carbon particles were significantly smaller than that of ZnO. So, the C particles could deposit on the surface of ZnO.

3.3 Photocatalytic Degradation of Dye Wastewater

The results of methylene blue removal under photolysis, adsorption, and photocatalysis are shown in Fig. 7. The results showed that the concentration of methylene blue was not significantly decreased for photolytic degradation (removal efficiency of 3%). For dark condition, the concentration of methylene blue was slightly decreased and the concentration was constant after 2 h (removal efficiency of 13%), while the concentration of methylene blue in the photocatalytic process was rapidly decreased. The removal efficiency at 3 h was 75%. It indicated that the modified photocatalysts with C solution can be used to degrade methylene blue under visible light irradiation with high efficiency.

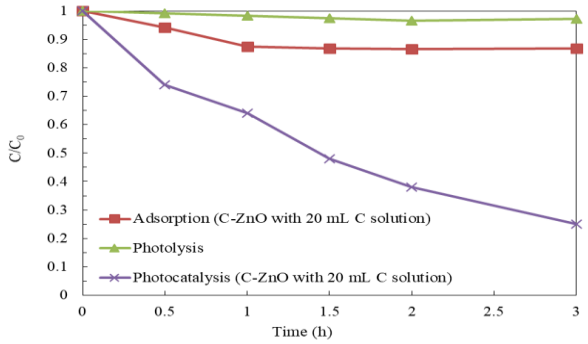

Fig. 6 Removal of methylene blue under different conditions (C_0 initial concentration of methylene blue(mg/L),C = remaining concentration of methylene blue at different time (mg/L))

Four different photocatalysts (pure ZnO, ZnO modified with C solutions (10, 20, and 30 mL) were used to study the effect of the initial quantity of C solution. Before photocatalytic experiments, the adsorption of methylene blue was carried out under the dark condition for 2 h. The adsorption of methylene blue reached equilibrium within 2 h for all photocatalysts. The photocatalyst with 30 mL C solution had the highest adsorption efficiency. After the adsorption process (2 h), the fluorescent daylight lamps (visible light) were turned on for photocatalytic degradation of methylene blue for 6 h. Fig. 7 showed that the methylene blue degradation rate versus reaction time under different C solution loading. The degradation rates of methylene blue by modified photocatalysts were significantly higher than that of pure ZnO, which improved to 30% (20 mL of C solution). The best photocatalytic degradation was ZnO modified with 20 mL of C solution (91%). Interestingly, as the C loading increased from 10 mL to 30 mL, the photocatalytic effect of the composites showed a phenomenon of first strengthening and then weakening. The reason is that some of the C dopants are agglomerated, so losing their effect on the photocatalytic performance gain as the C loading increases. Moreover, the too many loading of C dopants hinders the light-capturing and charge transferability of the surface of pure ZnO particles [16], so that the photocatalytic performance was lowered.

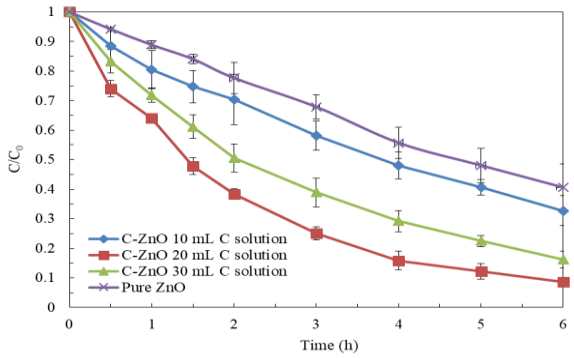

Fig. 7 Photocatalytic removal of methylene blue by synthesized photocatalysts with the various initial amounts of C solution (C_0 = initial concentration of methylene blue (mg/L), C = remaining concentration of methylene blue at a different time (mg/L))

4. Conclusions

Coffee ground was successfully used as the raw material to synthesize a C dopant for modification of the ZnO photocatalysts. The C particles derived from coffee ground could deposit on the surface of ZnO. So, the obtained C-modified ZnO had a hexagonal form like the wurtzite type, similar to the pure ZnO. Methylene blue solution was used as the model for dye wastewater. It was found that the adsorption of methylene blue reached equilibrium within 2 h under the dark. Photocatalytic degradation of dye wastewater was studied at various initial amounts of C solutions (10, 20, and 30 mL) to mix with ZnO powder. As the C loading increased from 10 mL to 30 mL, the photocatalytic effect of the composites showed a

phenomenon of first strengthening and then weakening. The best photocatalytic degradation was obtained on the C-modified ZnO with an initial C solution of 20 mL.

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